

One-parameter optimization of a nonempirical meta-generalized-gradient-approximation for the exchange-correlation energy

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The meta-generalized-gradient-approximation (meta-GGA) for the exchange-correlation energy, as constructed by Tao, Perdew, Staroverov, and Scuseria (TPSS) [Phys. Rev. Lett. **91**, 146401 (2003)], has achieved usefully consistent accuracy for diverse systems and is the most reliable nonempirical density functional (and the most reliable nonhybrid) in common use. We present here an optimized version of this TPSS functional obtained by empirically fitting a single free parameter that controls the approach of the exchange enhancement factor to its rapidly-varying-density limit, while preserving all the exact constraints that the original TPSS functional satisfies. We find that molecular atomization energies are significantly improved with the optimized version and are even better than those obtained with the best hybrid functionals employing a fraction of exact exchange (e.g., the TPSS hybrid), while energy barrier heights are slightly improved; jellium surface energies remain accurate and almost unchanged. The one-parameter freedom of the TPSS functional may be useful even beyond the meta-GGA level, since the TPSS approximation is a natural starting point for the higher-level hyper-GGA.

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I. INTRODUCTION

Kohn-Sham density functional theory [1] is a standard modern electronic structure theory. In this theory the exchange-correlation (xc) part of the energy, which includes all unknown many-body effects, must be approximated as a functional of the electron density $n(\mathbf{r})$. Although the exact form of the universal functional remains unknown, many exact properties of the functional have been discovered. Non-empirical functionals are developed from first principles by incorporating known exact constraints without fitting to data. The commonly used xc functionals can be assigned to the rungs of a ladder [2]. Higher rungs employ more local ingredients (which can be used to satisfy more exact constraints) and achieve higher accuracy. The first three rungs are semilocal and thus computationally efficient in selfconsistent-field calculations: the local spin density approximation (LSDA) [1], which only uses the local density as an ingredient, the generalized gradient approximation (GGA) [3], which employs not only the density but also the density gradient, and the meta-GGA [4–7], which further makes use of the Kohn-Sham orbital kinetic energy density. While the chosen GGA ingredients were originally motivated by the second-order gradient approximation, the meta-GGA ingredients were motivated by the fourth-order gradient expansion [8] of the exchange energy and the expansion of the exchange hole for small interelectronic distance [9]. Exact constraints on $E_{xc}[n]$ satisfied by the LSDA or by the nonempirical GGA [3] and meta-GGA [7] include the uniform-density limit, various scaling relations [10,11], and the Lieb-Oxford [12,13] bound.

A meta-GGA functional can be written as

$$E_{xc}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n \epsilon_{xc}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}), \quad (1)$$

where $n = n_{\uparrow} + n_{\downarrow}$ and τ_{σ} is the Kohn-Sham kinetic energy density of σ -spin electrons defined by

$$\tau_{\sigma}(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \varphi_{i\sigma}(\mathbf{r})|^2. \quad (2)$$

The $\varphi_{i\sigma}$ are the occupied Kohn-Sham orbitals.

Starting from the Perdew-Burke-Ernzerhof (PBE) GGA [3], Tao, Perdew, Scuseria, and Staroverov (TPSS) [7] have constructed a meta-GGA which satisfies all of the exact or nearly exact constraints satisfied by the PBE GGA, while adding more. The most important added constraints are as follows.

(i) The exchange part of the TPSS meta-GGA recovers the full fourth-order gradient expansion [8] in the limit of slowly varying density $n(\mathbf{r})$, and is exact for the hydrogen atom. It is designed so that its exchange potential $\delta E_x / \delta n_{\sigma}(\mathbf{r})$ remains finite [14] at the nucleus of an atom, where the PBE GGA potential improperly but weakly diverges.

(ii) Like the meta-GGA correlation energy of Perdew, Kurth, Zupan, and Blaha (PKZB) [6], the correlation part of the TPSS meta-GGA properly vanishes for any one-electron density.

(iii) The PBE-GGA exchange-correlation energy is properly almost independent of the relative spin polarization $\zeta = (n_{\uparrow} - n_{\downarrow})/n$ in the low-density limit. This good feature is lost in the earlier PKZB but restored in the TPSS functional.

Because the parameters introduced are fixed by exact constraints and not by fitting to experiment, nonempirical functionals are more transferable and accurate for diverse systems [15–22] than are empirical ones. High transferrability demands respect for two paradigms, one for condensed matter physics and another for quantum chemistry, because a general-purpose density functional should work for solids and solid surfaces as well as for atoms and molecules. The

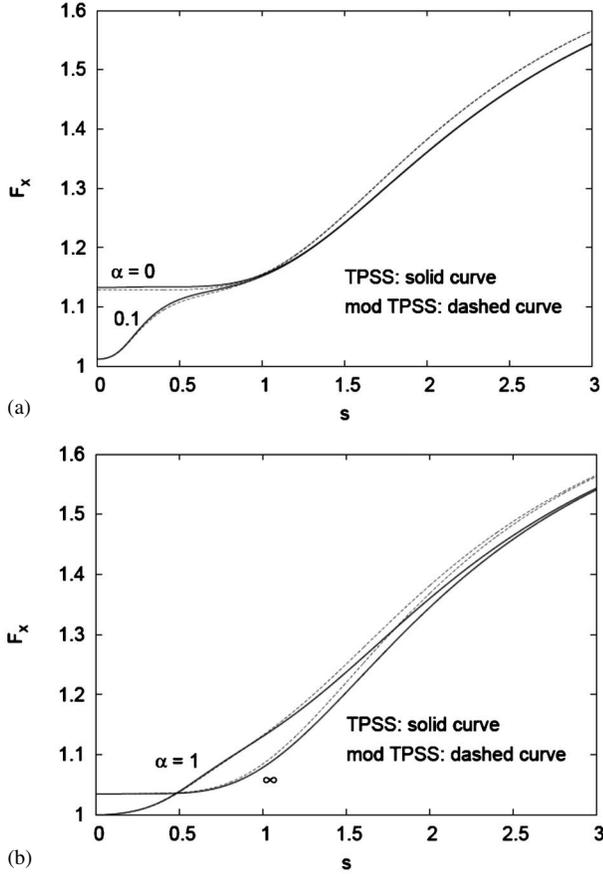


FIG. 1. (a), (b) TPSS and modified TPSS exchange enhancement factors F_x of Eq. (6) as functions of the reduced gradient s for various values of α . $\alpha=0$ is the iso-orbital (one- or two-electron) limit, while $\alpha=1$ approaches the slowly varying limit as $s \rightarrow 0$.

paradigm for condensed matter physics is embodied by the slowly varying limit, and the one for quantum chemistry by the one- or two-electron density. Both are respected in the TPSS approximation via their respective constraints.

In the development from PBE GGA to TPSS meta-GGA, the added constraints on the exchange energy apply only for small reduced density gradients. Thus there is no nonempirical reason to change from the PBE large-gradient behavior, and (unlike the case for PKZB) no such change was made. As we will show below, this choice was in a sense a nearly optimal one.

In the construction of the TPSS meta-GGA, several parameters were introduced and fixed by the imposed constraints. One of the parameters (μ), however, was determined by the requirement that in the approach to its large-gradient (rapidly varying) limit, TPSS exchange should recover the PBE GGA (i.e., that the TPSS meta-GGA and PBE GGA should agree to order $|\nabla n|^{-2}$ when $|\nabla n| \rightarrow \infty$). This requirement was intended to (and did) preserve the good PBE performance for bond lengths and other properties of hydrogen-bonded systems. In this paper, we relax this requirement and optimize this parameter by a fit to molecular atomization energies. We also confirm that this optimization essentially does not change the accurate jellium surface energy of the

original version of TPSS, because the surface energy is insensitive to the large-gradient behavior.

II. TPSS META-GGA

Since our optimization is made only in the exchange part of the TPSS functional, we will focus on exchange. Because of a simple spin-scaling relationship [11], we only need to consider the spin-unpolarized case.

We recall the exchange enhancement factor $F_x^{\text{PBE}}(s)$ for the PBE GGA [3], which gives the enhancement with respect to LSDA exchange as a function of the reduced density gradient s (defined below) and depends upon two parameters. The parameter μ controls the approach of F_x^{PBE} to its slowly varying or $s \rightarrow 0$ and rapidly varying or $s \rightarrow \infty$ limits (1 and $1 + \kappa$, respectively), while the parameter $\kappa = 0.804$ sets the large-gradient limit. (Satisfaction of the Lieb-Oxford bound on E_x for all possible densities requires $\kappa \leq 0.804$, and $\kappa = 0$ recovers LSDA linear response for the uniform gas, PBE chose $\mu = 0.21951$, which is about twice the value needed to recover the exact second-order gradient expansion, as discussed further below.

The TPSS exchange energy has the form

$$E_x^{\text{TPSS}}[n] = \int d^3r n \varepsilon_x^{\text{unif}}(n) F_x^{\text{TPSS}}(p, z), \quad (3)$$

where $\varepsilon_x^{\text{unif}}(n) = -3(3\pi^2 n)^{1/3}/4\pi$ is the exchange energy per electron for the uniform electron gas of density n , $p = s^2 = |\nabla n|^2/[4(3\pi^2)^{2/3}n^{8/3}]$ is the square of a dimensionless density gradient, and $z = \tau_W/\tau$ is an inhomogeneity parameter that arises beyond the GGA. Regions of one- or two-electron density may be recognized by the condition $\tau = \tau_W$, where $\tau_W = |\nabla n|^2/8n$ is the von Weizsäcker [23] kinetic energy density. The parameter z falls in the range $0 \leq z \leq 1$. $z = 1$ for one- and two-electron densities while $z = 5p/3 + O(\nabla^4) \rightarrow 0$ for slowly-varying densities, for which the kinetic energy density has a gradient expansion.

To construct F_x , TPSS introduced a variable \tilde{q}_b which combines p and z :

$$\tilde{q}_b = (9/20)(\alpha - 1)/[1 + b\alpha(\alpha - 1)]^{1/2} + 2p/3, \quad (4)$$

where

$$\alpha = (\tau - \tau_{vW})/\tau^{\text{unif}} = (5p/3)(z^{-1} - 1) \geq 0. \quad (5)$$

The parameter $b = 0.4$ in Eq. (4) is the smallest value that preserves F_x^{TPSS} as a monotonic function of p for each α ; this choice is made for esthetic reasons, since $b = 0$ produces nearly the same results in molecular tests. This expression for \tilde{q}_b becomes the reduced Laplacian q (as defined below) in the slowly varying limit, and $-9/20 + 2p/3$ in the iso-orbital ($\alpha = 0$) limit.

TPSS chose to retain the form of the PBE enhancement factor, but with μs^2 replaced by a function x , i.e.,

$$F_x^{\text{TPSS}} = 1 + \kappa - \frac{\kappa}{1 + \frac{x}{\kappa}}, \quad (6)$$

where

$$x = \frac{\left(\frac{10}{81} + c \frac{z^2}{(1+z^2)^2}\right)p + \frac{146}{2025}\tilde{q}_b^2 - \frac{73}{405}\tilde{q}_b \sqrt{\frac{1}{2}\left(\frac{3}{5}z\right)^2 + \frac{1}{2}p^2} + \frac{1}{\kappa}\left(\frac{10}{80}\right)^2 p^2 + 2\sqrt{e}\frac{10}{81}\left(\frac{3}{5}z\right)^2 + e\mu p^3}{(1 + \sqrt{ep})^2}. \quad (7)$$

The parameters c and e , which depend upon μ , are fixed by the last two constraints (i) of Sec. I. In the large-gradient limit,

$$\lim_{s \rightarrow \infty} x \rightarrow \mu s^2, \quad (8)$$

leading to agreement through order s^{-2} with the PBE enhancement factor (for reasons discussed at the end of Sec. I):

$$\lim_{s \rightarrow \infty} F_x^{\text{TPSS}} = 1 + \kappa - \frac{\kappa^2}{\mu s^2}. \quad (9)$$

For the slowly varying limit relevant to solids, the TPSS F_x recovers the fourth-order gradient expansion [8]:

$$F_x = 1 + \frac{10}{81}p + \frac{146}{2025}q^2 - \frac{73}{405}qp + Dp^2 + O(\nabla^6), \quad (10)$$

where $q = \nabla^2 n / [4(3\pi^2)^{2/3} n^{5/3}]$ is the reduced Laplacian of the density and $D=0$. The coefficient of the PBE second-order gradient term is too large, compared to the exact one $10/81$. This makes the PBE surface energy too low, while the TPSS surface energy is about right (as discussed in Sec. III).

We will demonstrate that improved atomization energies can be found from the TPSS functional by changing the approach to the large-gradient limit, i.e., changing the parameter μ in Eqs. (7)–(9) from its PBE value 0.219 51. Unlike the case for PBE, this change affects *only* the large- s and not the small- s behavior of the TPSS enhancement factor, as shown in Fig. 1.

III. RESULTS AND DISCUSSION

In the assessment or fitting of density functionals, great weight is often given to their performance for test sets of molecular atomization energies [24–28]. For a quick evaluation of density functionals for thermochemistry or kinetics, we use the AE6 and BH6 test sets of Lynch and Truhlar [24]. The AE6 set of atomization energies includes six molecules: SiH₄, S₂, SiO, C₃H₄ (propyne), C₂H₂O₂ (glyoxal), and C₄H₈ (cyclobutane). The BH6 set of barrier heights consists of the forward and reverse barriers for three reactions: OH+CH₄ → CH₃+H₂O, H+OH → H₂+O, and H+H₂S → H₂+HS. These test sets, although small, are quite diverse and were constructed to reproduce errors in much larger sets. It is important to have such representative test sets to avoid false conclusions about the accuracy of the functional that might be reached from small but unrepresentative sets.

The TPSS functional is extremely accurate [16,18] for the enthalpies of formation calculated from atomization energies of the large G3/99 thermochemical test set of Curtiss *et al.* [27]. This good performance is further improved signi-

ficantly by our optimal parameter sets. In this paper we use the procedure developed for G3X theory [28], which uses minus the calculated atomization energies at the Becke three-parameter Lee-Yang-Parr hybrid functional (B3LYP)/6-31G(2df,p) equilibrium geometries, the B3LYP/6-31G(2df,p) zero-point energies with a frequency scale factor of 0.9854, scaled molecular thermal corrections, and experimental atomic data. Comparison of Tables I and II shows that the AE6 test set is qualitatively representative for the 223 enthalpies of the G3/99 test set (the COF₂ molecule was kept in the test set), but quantitative differences occur as the improvement is considerably larger for the enthalpies of the G3/99 test set using our modified TPSS parameters. The origin of these differences is not the difference in the basis sets (see below). The 223 enthalpies of formation can be grouped into three subsets, designated as G2-1, G2-2, and G3-3 that contain 55, 93, and 75 molecules, respectively [29]. The G2-1 and G2-2 subsets form the G2/97 set that contains 148 molecules. The critically evaluated experimental data of the G3/99 set make it a useful calibration tool for density functional methods. The G3-3 subset is particularly interesting. This subset includes larger organic molecules (up to ten carbon atoms, like azulene) and several difficult-to-calculate inorganic molecules (like PF₅, PCl₅, S₂Cl₂; cf. Table II). It has been observed [16] that empirical density

TABLE I. Deviations from experiment of the AE6 [24] molecular atomization energies obtained from the modified TPSS meta-GGA, with several different parameter sets. All calculations were performed self-consistently with the 6-311+G(3df,2p) basis set. The first row is the original TPSS parameter set (more precisely 0.219 51, 1.537, and 1.590 96). Shown are mean error (ME), mean absolute error (MAE), root mean square (rms) error, and standard deviation. All energies in kcal/mol (1 hartree=627.5 kcal/mol). (The mean AE6 atomization energy is 517.2 kcal/mol. For comparison, the MAE's of LSDA, PBE, and PBE global hybrid functionals with 25% exact exchange are [31] 77.3, 15.5, and 6.2 kcal/mol, respectively.) The parameter values for minimal MAE are boldfaced.

μ	e	c	Atomization energy			
			ME	MAE	rms	Std. Dev.
0.220	1.54	1.59096	4.13	5.92	6.61	5.66
0.225	1.51	1.55384	3.65	5.55	6.35	5.69
0.230	1.48	1.51988	3.23	5.22	6.14	5.72
0.240	1.43	1.45660	2.40	4.58	5.84	5.80
0.250	1.38	1.39660	1.62	4.42	5.68	5.96
0.252	1.37	1.38496	1.47	4.43	5.66	5.99
0.260	1.33	1.33976	0.88	4.50	5.65	6.11

TABLE II. Deviations from experiment of the G3/99 [27] standard molecular enthalpies of formation obtained from the modified TPSS meta-GGA, with several different parameter sets. The G3/99 test set (223 molecules) consists of three subsets called G2-1 (55 small molecules), G2-2 (93 larger molecules), and G3-3 (75 relatively large organic molecules and radicals). The geometries, thermal corrections, and zero-point energies were obtained at the B3LYP/6-31G(2df,p) level using a frequency scale factor of 0.9854 [28,29]. All calculations were performed self-consistently with the 6-311++G(3df,3pd) basis set. The first row is the original TPSS parameter set (more precisely 0.219 51, 1.537, and 1.590 96). Shown are mean error (ME), mean absolute error (MAE), root mean square (rms) error, standard deviation, maximal positive error [Max(+)], maximal negative error [Max(-)], and the related molecules. All energies in kcal/mol. (1 hartree = 627.5 kcal/mol.) Error=theory-experiment. The mean experimental atomization energies for the G2-1, G2-2, and G3-3 sets are about 220, 670, and 1180 kcal/mol, respectively.

μ	e	c	Set	ME	MAE	Standard molecular enthalpies of formation					
						rms	Std. Dev.	Max(+)	Max(-)		
0.220	1.54	1.59096	G2-1	-3.66	4.47	2.83	4.40	5.6	(SiO)	-17.9	(Si ₂ H ₆)
			G2-2	-6.13	6.88	5.12	5.06	16.2	(SiF ₄)	-22.9	(ClF ₃)
			G3-3	-5.19	5.48	3.58	3.36	7.5	(PF ₅)	-12.8	(S ₂ Cl ₂)
			G3/99	-5.20	5.81	6.86	4.48	16.2		-22.9	
0.250	1.38	1.39660	G2-1	-2.55	3.97	2.53	4.44	7.3	(SiO)	-15.6	(Si ₂ H ₆)
			G2-2	-2.64	4.26	3.82	5.33	21.7	(SiF ₄)	-19.9	(ClF ₃)
			G3-3	1.25	3.08	2.27	3.74	14.2	(PF ₅)	-10.6	(S ₂ Cl ₂)
			G3/99	-1.31	3.79	5.12	4.96	21.7		-19.9	
0.252	1.37	1.38496	G2-1	-2.49	3.95	2.51	4.44	7.4	(SiO)	-15.4	(Si ₂ H ₆)
			G2-2	-2.43	4.15	3.78	5.35	22.1	(SiF ₄)	-19.6	(ClF ₃)
			G3-3	1.64	3.29	2.39	3.80	14.6	(PF ₅)	-10.5	(S ₂ Cl ₂)
			G3/99	-1.08	3.81	5.13	5.02	22.1		-19.6	

functionals such as B3LYP that are calibrated and perform well on the G2/97 test set can fail seriously on the G3-3 subset, but this is not necessarily true for the other functionals.

Like all standard semilocal functionals, the TPSS is not accurate for barrier heights. In comparison with PBE, the TPSS functional greatly improves molecular atomization energies and solid surface energies [17], although it only slightly improves barriers.

In our modified TPSS functional, we increased the parameter μ above 0.21951, adjusting the parameters e and c to retain the conditions for the exact exchange energy of the ground-state hydrogen atom and $dF_x/ds=0$ at $s=0.376$ for $z=1$. The latter condition keeps the meta-GGA exchange potential finite at the nucleus for one- and two-electron atoms. Five different parameter sets were considered. All molecular calculations were performed self-consistently with the developmental version of the GAUSSIAN suite of programs [30] with the 6-311+G(3df,2dp) basis set. In Table I, we also show the parameters ($\mu=0.252$, etc.) that minimize a parabolic fit to the MAE values of the AE6 atomization energies at $\mu=0.240$, 0.250, and 0.260. We see in Table I that an increase of μ above the original 0.219 51 leads to better atomization energies. The best results were obtained with the parameter set $\mu=0.250$, $e=1.38$, and $c=1.3966$, which somewhat reduces the typical TPSS overbinding of molecules. Note that the parameter set $\mu=0.252$, $e=1.37$, and $c=1.384 96$ reduces slightly further the TPSS overbinding tendency at the expense of a very slightly increased MAE (cf. the MEs in Tables I and II). We have also tested the use of PBE GGA orbitals [31] and the resulting energy differences agree with fully converged and fully self-consistent ones.

Our results in Table II show that the quite good performance of the original TPSS for the G3/99 test set and its G3-3 subset is further improved by our new TPSS parameters. For the G3-3 subset the modified TPSS clearly outperforms even the hybrid methods, like the B3LYP, the Becke three-parameter Perdew-Wang 1991 (B3PW91), and the TPSSh [16] functionals with MAEs=8.44, 4.87, and 3.33 kcal/mol, respectively (cf. 3.08 kcal/mol for the modified TPSS in Table II). The typical overbinding of TPSS is turned into a rather small G3-3 underbinding in the modified TPSS functional. We note that the performance of the modified TPSS for the G3-3 subset is even better with the 6-311+G(3df,3dp) basis set (no diffuse functions on the H atoms) with AE and MAE equal to 0.40 and 2.69 kcal/mol, respectively. We have also tested the 6-311+G(3df,2p) basis set that gave very similar results (with the parameter set $\mu=0.250$, $e=1.38$, and $c=1.3966$: ME=-1.29 kcal/mol, MAE=3.81 kcal/mol for the G3/99 test set, agreeing within 0.02 kcal/mol with the values in Table II). Mixing modified TPSS with 10% exact exchange as in Ref. [16] (global hybrid) deteriorates the results considerably, leading to general underbinding (ME=2.4 kcal/mol, MAE=4.7 kcal/mol for the G3/99 test set), and increases the computational time for the test by about 150%. We observed that the standard GAUSSIAN [30] integration grid size is sufficient, and the use of the expensive ultrafine grid is not necessary in these calculations. With these modifications, 25% of the computational time can be saved for the G3/99 test set with insignificant loss of precision. This observation suggests using the more economical 6-311+G(3df,2p) basis set instead of the expensive 6-311++G(3df,3pd) basis set for testing purposes.

TABLE III. Deviations from experiment of the BH6 barrier heights [24] obtained from the modified TPSS functional, with several different values of μ , with e and c as in Table I. All calculations were performed self-consistently with the 6-311+G(3df,2p) basis set. The first row is the original TPSS. All energies in kcal/mol. (The mean BH6 barrier height is 11.8 kcal/mol. LSDA, PBE, and PBE hybrid barrier MAE's are [31] 17.9, 9.5, and 4.8 kcal/mol, respectively.)

μ	ME	Barrier MAE	rms
0.220	-8.45	8.45	8.76
0.225	-8.37	8.37	8.69
0.230	-8.30	8.30	8.63
0.240	-8.16	8.16	8.51
0.250	-8.03	8.03	8.40
0.252	-8.00	8.00	8.38
0.260	-7.90	7.90	8.29

Common semilocal density functionals underestimate the energy barrier heights for chemical reactions [32–34]. The source of this error is the transition-state energy, which is generally relatively too low with semilocal functionals. The transition state can be considered as a weakly bound system where bonds are being broken and formed. As we can see from Table III, our modified TPSS results for reaction barrier heights show a small improvement over the original TPSS; the best barriers we calculated were for the parameter set $\mu=0.260$, $e=1.33$, and $c=1.33976$. The parameter set that optimizes the atomization energies also improves the energy barriers, but only slightly. To reduce the remaining reaction-barrier error of any version of the TPSS functional requires a partial (global hybrid) or full self-interaction correction [32–34].

For a solid, the bulk energy is the energy per unit volume, and the surface energy is the energy per unit area needed to cut the bulk along a plane. Calculations of surface energies of solids within the LSDA show reasonable agreement with experimental results. The good-quality LSDA surface energies arise from a cancellation of errors between exchange and correlation terms. The individual errors of exchange and correlation surface energies are reduced by the PBE and TPSS functionals, but in PBE the summed exchange-correlation energy is lower and less accurate than in the LSDA, while in TPSS it is a little higher and more accurate [35], at least for the jellium model.

In the jellium model of a bulk metal, the ionic lattice is replaced by a uniform positive-charge background of density $n=3/(4\pi r_s^3)$. In the jellium model of a planar surface, this background terminates sharply at a plane. Table IV shows the exchange-correlation jellium surface energy for four different r_s values, obtained with different values of μ . The results of Table III confirm that the optimization of TPSS for molecular atomization energies does not degrade the good-quality TPSS surface energies. The change in the surface energy is negligible for any considered value of μ compared to the likely error of the original TPSS value.

TABLE IV. Exchange-correlation (xc) surface energies of jellium for four bulk density parameters r_s , from the modified TPSS functional, with several different values of μ , with e and c as in Table I. All calculations employ LSDA orbitals defined on a numerical grid. The first row is the original TPSS. All surface energies are in erg/cm². (1 hartree/bohr²=1.557×10⁶ erg/cm².)

μ	Surface xc energy			
	r_s			
	2	3	4	6
0.220	3380	772	266	55.5
0.225	3380	772	266	55.5
0.230	3380	772	266	55.4
0.240	3380	772	265	55.3
0.250	3380	771	265	55.2
0.252	3380	771	265	55.2
0.260	3380	771	265	55.1

In Figs. 1(a) and 1(b), we have plotted the exchange enhancement factor of the optimized TPSS functionals (with $\mu=0.252$, $e=1.37$, and $c=1.38496$) and compared it to the original TPSS enhancement factor for several values of α in the physical range of $0 < s < 3$. We can observe from the figure that our optimized version differs noticeably from the original TPSS only when $s > 1$. That is why the TPSS surface energies of Table IV are not changed significantly by the optimization. The bulk properties of solids [17] should not be significantly changed either; the large- s domain affects mainly the atomization energies.

The change in the parameter μ , from the original TPSS 0.21951 to the optimized or modified 0.252, is not large, suggesting that the original and nonempirical TPSS meta-GGA is already nearly optimized. Even hydrogen bonds [16], which are sensitive to the approach to the large-gradient limit, should not be much changed. The parameter κ in Eq. (9) is already optimal; increasing κ above 0.804 would also reduce and improve TPSS atomization energies as it reduces and improves PBE atomization energies [36], but would in either case violate the Lieb-Oxford bound for some possible densities.

In summary, we have made a one-parameter empirical optimization of the TPSS meta-GGA, leading to a considerable improvement over the original TPSS in molecular atomization energy and a small improvement in energy barrier height. Comparison of our G3 atomization energies with those from 18 standard functionals in Table I of Ref. [16] shows that our modified TPSS outperforms even the standard hybrid functionals that mix in a fraction of exact exchange with the help of one or more empirical parameters. We confirm that our optimization essentially does not change the good TPSS surface energy, and we suspect that it will not change the TPSS bulk properties of solids either. We continue to recommend use of the well-tested [16–22] original TPSS functional, except for problems where more accurate molecular atomization energies are needed; for such problems, we recommend our modified TPSS version.

Finally, we observe that the TPSS meta-GGA is a natural input to the higher-level hyper-GGA [2,37], for which the

one-parameter freedom proposed here may also be useful. (It is for the sake of such possible future applications that we have shown in Table I how the dependent parameters e and c vary with the independent one μ .) The added ingredient of a hyper-GGA (local hybrid or fourth-rung functional) is the exact exchange energy density. As we have argued elsewhere [37], hyper-GGA's can satisfy many more exact constraints than meta-GGA's, but require one or more empirical parameters.

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